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Sputter deposition of TiNi, TiNiPd and TiPd films displaying the two-way shape-memory effect

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Abstract

TiNi, TiNiPd and TiPd films exhibiting the one-way and two-way shape-memory effect have been prepared by d.c. magnetron sputtering onto unheated substrates followed by annealing and training processes. In the case of TiNi, films could be prepared showing the R-phase transition, the important feature of which is its small hysteresis of about 1 K. By the Ni–Pd substitution the transition temperatures (austenite/martensite finish temperatures) could be increased from 32 °C/−38 °C for the binary NiTi alloy to a maximum of 570 °C/498 °C for TiPd films. The films have been subject to further microstructuring for developing micro-actuators displaying the two-way shape-memory effect.

Keywords: Shape-memory effect; Smart materials; Sputter deposition; Ti(Ni,Pd) films

1. Introduction

The availability of suitable actuators is particularly important for the advanced development of new or improved microsystems. The traditional concept of down-scaling of successful macroscopic actuators shows the important drawback that some physical properties, e.g., friction, do not scale linearly with the dimension [1]. An attractive alternative approach is based on smart materials that directly transduce electrical into mechanical energy, e.g., materials exhibiting shape-memory effects, piezoelectricity or magnetostriction. In the development of actuators based on these smart materials, the principles that allow easy down-scaling to the micrometre range and can be realized by a cost-effective manufacturing technique compatible with microsystem technology are of special interest. As a consequence, thin-film technologies have received more attention.

As shape-memory alloys combine high output forces with large motions and can be controlled by Joule heat in a microelectronic-compatible way, they are of increasing interest for micro-actuator applications [2,3]. Due to smaller grain sizes (1–2 μm) compared with those of bulk materials, magnetron sputter deposition allows the realization of shape-memory thin films in the range of 2 to 20 μm thickness. Furthermore, these films can be easily integrated into microsystem process technology.

Binary thin-film TiNi has been developed using different techniques like d.c. or r.f. magnetron sputtering [4–7], ion beam sputtering [8] or laser ablation [9]. Some limitations are given by the low transition temperatures of <60 °C/140 °C (martensite/austenite finish temperature, respectively) [4] in combination with large hysteresis for NiTi films exhibiting no intermediate R-phase transition, and even lower temperatures (<50 °C) for Ni-rich films showing the R-phase transition with its narrow hysteresis [4,10]. In order to reduce hysteresis, films of the ternary alloy Ti(NiCu) have been investigated [11], but due to their low Ti content, these films only show transition below 300 K. As higher transition temperatures are needed for higher actuation speed as well as for applications at higher ambient temperatures, e.g., automotive applications, an increase of these transition temperatures achieved by partial or total substitution of Ni by Pd was studied for films showing the two-way effect.

2. Experimental

Based on results of sputtered TiNi films, Ti-rich targets (Ti content of 54 at.%) with different Ni/Pd ratios were produced by hot pressing. Films were formed by d.c. magnetron sputter deposition onto unheated SiO_2 substrates, then

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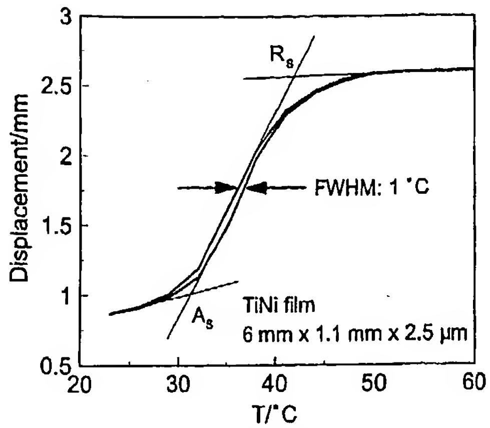

Fig. 1. Beam-bending characteristics of a TiNi film upon cooling and heating. The R-phase transformation temperatures and the half width of the hysteresis are indicated.

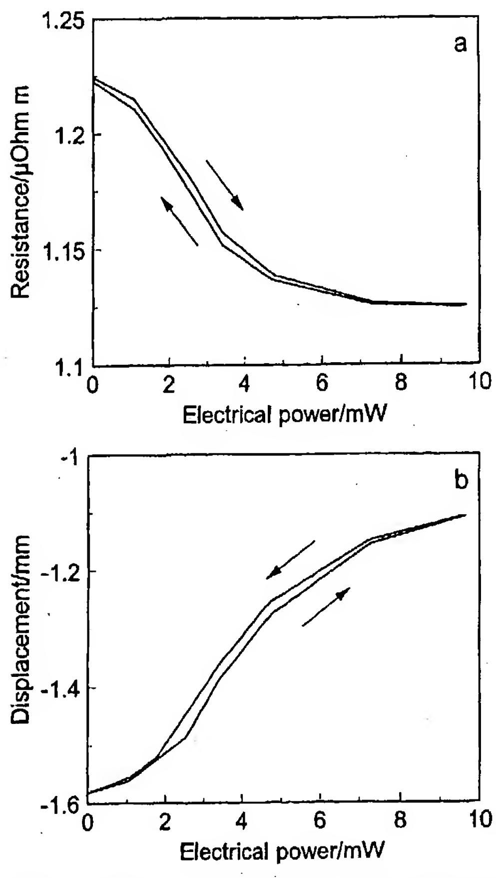

Fig. 2. Electrical resistance (a) and bending (b) characteristics of a 8 μm NiTi thin-film device obtained in air by resistive heating control.

crystallized at 750 °C, annealed at 450 °C for 1 h and trained for the two-way (or all-round) effect [7]. Typical deposition rates, with an argon sputtering pressure of 0.4 Pa, are ≈ 10 $\mu m\ h^{-1}$ at 300 W and a distance of 50 mm.

The composition was determined by wavelength- or energy-dispersive X-ray microanalysis (WDX, EDX), and depth profiles were obtained using Auger electron spectroscopy (AES). The microstructures were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Transition temperatures were determined by differential scanning calorimetry (DSC) and electric resistance measurements. Double-beam micro-actuator devices have been realized by electrolytic photoetching or by mask-sputtering. Their mechanical properties were measured by beam-bending experiments as a function of ambient temperature or resistive heating current.

3. Results and discussion

3.1. TiNi films

Shape-memory TiNi films with different compositions were subsequently fabricated by d.c. magnetron sputtering onto unheated substrates, by removal of the substrates in order to get freestanding films, and by special heat treatment as a training for the two-way effect [7]. This results in films with oriented Ti_3Ni_4 precipitates (X-phase) which work as an inner bias spring [10]. Of special interest are TiNi films exhibiting the intermediate R-phase transition. Characterization by beam-bending experiments reveals the R-phase transition at ≈ 35 °C (Fig. 1) and its small hysteresis, which

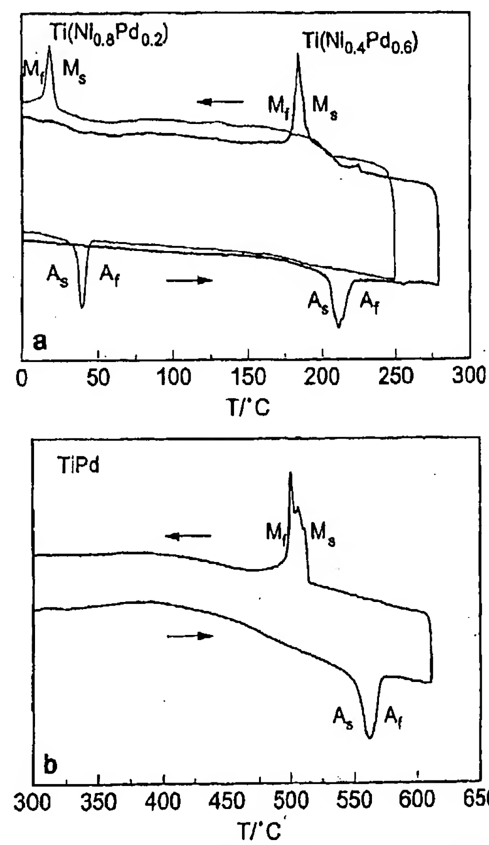

Fig. 3. Cyclic thermal characterization (M_s, M_f, A_s, A_f: martensite and austenite start and finish temperatures, respectively) of Ti(NiPd) (a) and TiPd (b) films by differential scanning calorimetry (DSC).

Table 1
Transition temperatures of different shape-memory films determined by DSC measurements (Fig. 3)

	M_f (°C)	M_s (°C)	A_s (°C)	A_f (°C)
TiNi	−38	7	24	32
$Ti(Ni_{0.8}Pd_{0.2})$	14	26	32	45
$Ti(Ni_{0.4}Pd_{0.6})$	179	192	203	220
TiPd	498	514	552	570

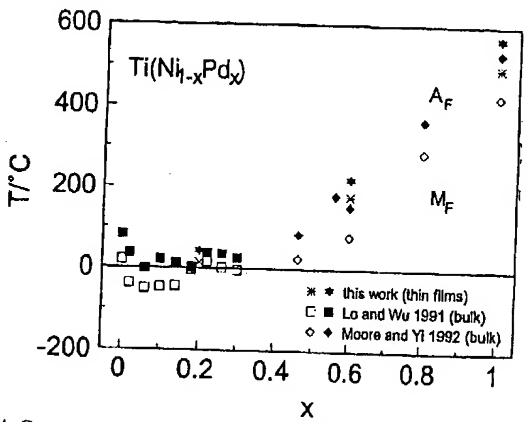

Fig. 4. Comparison of transition temperatures (M_f, A_f: martensite and austenite finish temperatures) of bulk [11,12] and thin-film $Ti(Ni_{1-x}Pd_x)$.

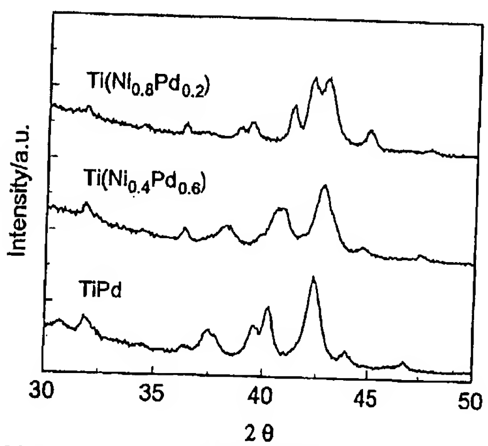

Fig. 5. Major X-ray diffraction peaks of TiNiPd and TiPd films exhibiting the two-way shape-memory effect.

is only slightly increased in the case of applied forces. This small hysteresis enables the fabrication of higher-speed actuators as well as of regulated actuators without the need for a complex control algorithm. In order to obtain maximum work output, the devices have to be operated at complete transformation cycles. This requires effective heating and cooling of the device regions of maximum strain. In particular, these general criteria have been met for thin-film devices. Small device cross sections and high surface-to-volume ratios provide effective heating at minimum currents and homogeneous, fast cooling of the micro-actuators. Fig. 2 shows the electrical resistance and bending characteristics as a function of the applied electrical power for an 8 μm NiTi thin-film device.

3.2. *TiNiPd and TiPd films*

The dependency of the transition temperatures upon the Ni/Pd ratio was investigated for two different TiNiPd compositions and compared to TiNi and TiPd. The transition temperatures, which were determined by DSC measurements with a heat flow of 10 K s^{-1} (Fig. 3), are summarized in Table 1.

These results demonstrate that a transition-temperature range of the shape-memory films between approximately room temperature (R.T.) and 500 °C can be covered by a suitable adjustment of the Pd content. The measured temperatures correspond well to those of bulk materials [12,13] (Fig. 4), but, at the same time represent the highest values ever realized for thin films.

From X-ray diffraction data (Fig. 5) the phase distributions and the lattice constants of the TiNiPd and TiPd films were determined at R.T. A Rietvold method for the simultaneous refinement of structure and size-strain parameters was used as the reflections were broad and overlapping [14]. Table 2 summarizes the obtained data.

The obtained data indicate that partial substitution of Ni by Pd leads to an increase of the lattice constant of the austenite phase B2, whereas the martensitic B19 phase is only slightly influenced by the Ni/Pd ratio.

The microstructure of $Ti(Ni_{0.8}Pd_{0.2})$ films investigated by transmission electron microscopy (TEM) after crystallization and aging consists of austenitic B2 grains about 1–2 μm in diameter (Fig. 6). The precipitates inside the B2 grains and along the grain boundaries are a Ti-rich phase with a Ti_2Ni-type lattice. Parts of the B2 grains exhibit R-phase diffraction spots in electron diffraction. $Ti(Ni_{0.4}Pd_{0.6})$ films are fully martensitic at R.T., as can be seen in Fig. 7. The grain boundaries can hardly be identified. Large Ti-rich precipitates along the grain boundaries show a Ti_2Pd-type lattice in electron-diffraction patterns.

Binary TiPd thin films exhibit roughly the same microstructure as the Pd-rich ternary $Ti(Ni_{0.4}Pd_{0.6})$ films. The grains are fully martensitic at R.T. after crystallization (Fig. 8). Strong twinning inside the martensite variants can be observed due to a more recovered microstructure compared to $Ti(Ni_{0.4}Pd_{0.6})$ and there are Ti_2Pd-precipitates along the grain bounderies.

4. Micro-actuators

The optimized shape-memory films are the basic material for the development of micro-actuators, which have been realized via microfabrication and subsequent packaging and interconnecting technologies. Fig. 9 shows a thin-film device microfabricated by electrolytic photoetching [2], and Fig. 10 a double-frame image of a mask-sputtered double-beam

Table 2
Phase distributions and the lattice constants of different shape-memory films determined by X-ray diffraction at R.T. (Fig.5)

	B2	B19′	B19	(Ti_2Ni):fcc	$(PdTi_2)$:$MoSi_2$
$Ti(Ni_{0.8}Pd_{0.2})$	$a=0.3015$ nm 80 vol.%	$a=0.3083$ nm $b=0.4968$ nm $c=0.4294$ nm $\gamma=99.4°$ 7 vol.%		$a=1.1393$ nm 13 vol.%	
$Ti(Ni_{0.4}Pd_{0.6})$			$a=0.4459$ nm $b=0.2811$ nm $c=0.4739$ nm 96 vol.%		$a=0.3080$ nm $c=0.9685$ nm 4 vol.%
TiPd	0.3196 nm 9 vol.%		$a=0.4594$ nm $b=0.2789$ nm $c=0.4893$ nm 83 vol.%		$a=0.3078$ nm $c=1.0045$ nm 8 vol.%

Fig. 6. TEM micrograph of a crystallized and aged $Ti(Ni_{0.8}Pd_{0.2})$ film: austenitic B2 grains with precipitates inside and along the boundaries.

Fig. 7. TEM micrograph of a crystallized and aged $Ti(Ni_{0.4}Pd_{0.6})$ film: due to the higher Pd content it is fully martensitic at R.T. with Ti_2Pd-type precipitates along the grain boundaries.

device at different ambient temperatures. The performance of these devices was tested by measuring the force–bending characteristics versus temperature (Fig. 11). These results reveal that the maximum work output for bending actuation of the shape-memory thin films of about 10^5 J m^{-3} is very promising for micro-actuator applications.

5. Conclusions and outlook

The high transition temperatures achieved enable the production of actuators suitable for greater temperature ranges as well as actuators for higher-frequency applications, as the cooling rates at higher operation temperatures will increase and therefore the response times will decrease. On the other hand, films exhibiting the R-phase transition are well suited

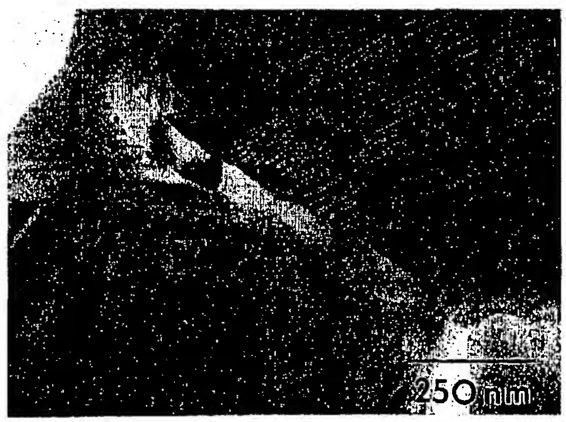

Fig. 8. TEM micrograph of a crystallized TiPd film: fully martensitic at R.T. with large Ti_2Pd-type precipitates along the grain boundaries.

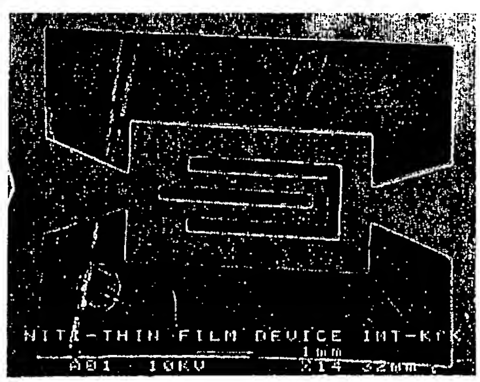

Fig. 9. SEM micrograph of a TiNi thin-film double-beam device. The process steps are electrolytic photoetching and subsequent cutting.

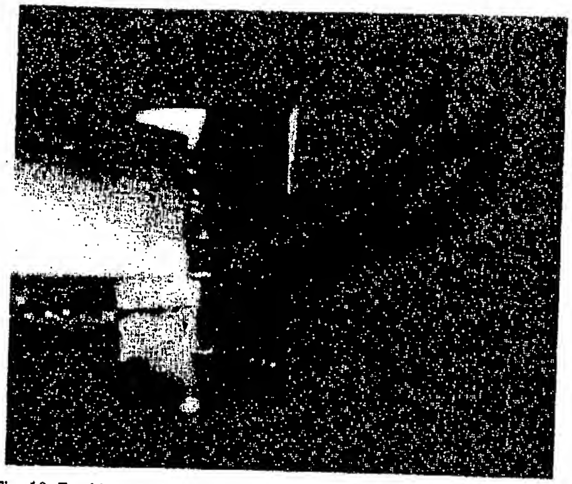

Fig. 10. Double-frame image of a TiNi double-beam cantilever at different ambient temperatures (R.T., 50°C) fabricated by mask-sputtering.

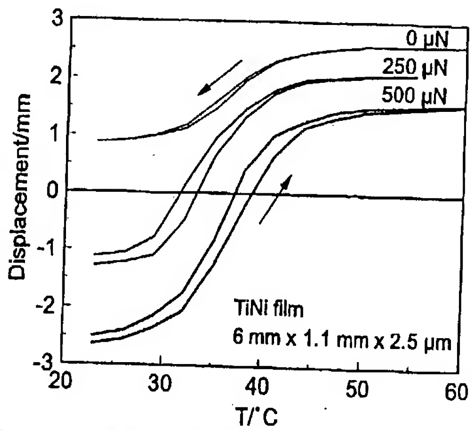

Fig. 11. Load-dependent beam-bending characteristics of a TiNi film upon cooling and heating.

for position-controlled actuator applications as their position can be read out directly by their specific electrical resistance.

Future directions in development will be oriented to materials improvement such as reduction of hysteresis and increase of the fatigue strength as well as to aspects of inexpensive and repeatable mass-production.

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Biographies

E. Quandt received his Dr.-Ing. in 1990 from the Technical University Berlin, where he worked on analytical electron microscopy. Since 1991 he has been responsible for the development of thin films as actuators in microsystem technology at the Institute of Materials Research of the Forschungszentrum Karlsruhe.

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H. Holleck, Dr.phil.habil., is head of the thin-film group in the Institute of Materials Research of the Forschungszentrum Karlsruhe and professor of materials science at the University of Karlsruhe. He has been at the Forschungszentrum Karlsruhe since 1965 working on materials science and thin-film technology.

K. Feit studied materials science at the Universities of Saarbrücken and Hamburg-Harburg. In 1990 he received his Ph.D. in polymer physics at the Technical University of Hamburg-Harburg. Since 1989 he has been head of a research group working on materials research at the Institut fur Mikrostrukturtechnik at the Forschungszentrum Karlsruhe. His current interests are material properties and development of testing methods for microstructures.

M. Kohl received his Ph.D. in physics from the University of Stuttgart in 1989. In 1990–1991 he was working as an IBM post-doctoral fellow at the T.J. Watson Research Center in Yorktown Heights (USA) and later joined the Forschungszentrum Karlsruhe. His main interests are low-dimensional material systems, microoptics and micromechanics. He is now head of a research group at the Institut fur Mikrostrukturtechnik working on the development of microactuators based on the LIGA process as well as the exploration of new intelligent materials for microsystems applications.

P. Schloßmacher received his Ph.D. in physics from the RWTH Aachen in 1991 for TEM studies on defects in GaAs. Since then he has been with the Institute of Materials Research of the Forschungszentrum Karlsruhe working on the field of TiNi-based shape-memory alloys and analytical/high-resolution TEM in general.

A. Skokan (Dr.rer.nat., University of Bonn, 1972) has been a scientific staff member of the Institute of Materials Research of the Forschungszentrum Karlsruhe since 1974. His current interests include thin-film characterization by microbeam analysis and X-ray diffraction.

K.D. Skrobanek received his diploma in mechanical engineering from the University of Karlsruhe in 1994 with an emphasis on laser patterning of shape-memory alloys. He is now working on his thesis at the Institut fur Mikrostrukturtechnik of the Forschungszentrum Karlsruhe in the field of design, fabrication and characterization of microcomponents with shape-memory effect.